USGS

WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: Fingerprinting Organic Material in the Caribou-Poker Creek Watershed to Support Hydrologic Investigations

Focus Categories: WQL, HYDGEO

Keywords: Hydrogeology, Organic Compounds, Water Quality Monitoring, Groundwater Quality

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Introduction

The Caribou and Poker Creek Watershed has become established as an important component of the Bonanza Creek LTER (Long Term Ecological Research) Program. A primary task of the LTER is to maintain reliable meteorological and hydrological measurements for use by any investigator upon request. In addition, process studies on interactions of hydrology, meteorology and permafrost are being conducted. Some preliminary studies have shown that the organic matter concentration in the streams is unusually high. By characterizing the nature and origin of organic matter in water below or above permafrost, in interpermafrost springs and in streams we can better describe the hydrology in regions of discontinuous permafrost. In addition to a better understanding of the hydrology of permafrost watersheds, understanding the origin of organic matter is important for drinking water treatment and use. Many public drinking water systems in Alaska extract water from above and below permafrost. Depending on the origin of the organic matter, certain health risks may be present.

Natural organic matter (NOM) in drinking water is a health concern because it contributes to the formation of disinfectant by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs). NOM causes other health, economic, and aesthetic problems since contaminants such as metals, hydrophobic organic chemicals, and radionuclides can be transported by NOM. Not all NOM has the potential to cause health risks, however. In order to evaluate the impact of organic matter on drinking water the hydrology should be considered. The CPCRW provides an excellent opportunity to investigate the NOM as it relates to hydrology in a well studied, discontinuous permafrost environment.

Characterization of NOM

The simplest method used to characterize NOM is organic carbon concentration in mg/L, either as TOC or DOC, or by UV absorbance at 254 nm (UV-254). Unfortunately, the bulk quantification of NOM as DOC or TOC provides no information about the composition of the organic matter (e.g., sugars, proteins, lignin). White and Beyer (1999) used pyrolysis-GC/MS fingerprinting to correlate the organic material found in subsurface antarctic soils to its surface origin. The research proposed herein will use the method of White and Beyer to correlate DOC in streamwater samples to water sources above and below permafrost as well as in interpermafrost springs.

Goals

Hypotheses

The outcome of this project relies on the central hypothesis that DOC in water can be correlated to upstream sources using the rapid fingerprinting technique, pyrolysis-G/MS. It follows that pyrolysis-GC/MS fingerprinting of organic matter will be used to estimate the origin of surface water contributing to groundwater and vice versa at different times during the course of the summer.

The researchers hypothesize that the NOM fingerprint from the high slope groundwater wells and springs will be well correlated to each other but distinctively different from the NOM fingerprint of stream water. It is expected that since stream NOM has a groundwater component, the fingerprint of the groundwater will be present in the stream water but masked by the NOM originating in the stream.

Objective

The hypotheses will be tested by collecting and analyzing water samples from the CPCRW over the course of one year. The organic matter in samples of 18 different water sources will be fingerprinted and cross-correlated. Based on correlations, the level of contribution by groundwater to surface water will be approximated.

Experimental Methods and Procedures

Site Selection

The CPCRW will be used as the site for investigation. Water samples will be selected from the 18 sites highlighted on Figure 1.

Site Selection

The CPCRW will be an ideal research watershed as the site for investigation. Water samples will be selected from six wells and stream/spring sampling from three different permafrost conditions of sub-watershed (C2, C3, and C4) as highlighted on the Figure 1. The graduate student will collect all water samples on this project under the direction of Dr. Kenji Yoshikawa.

Well MD

Site MD is the base of the northeast facing slope on the Helmer's Ridge at an elevation of 313m (65º10'26.59572"N, 147º30'57.55878"W). The site consists of two wells, MD1 and MD2, located 5m apart, parallel to the slope. MD1 (130' deep) is for the ground temperature observation. MD2 (70' deep) is for the ground water observation purpose. The vegetation at the site consists of open black spruce forest (*Picea mariana*) and with 37cm organic mat of feather mosses and sphagnum. The site slopes 5º to 70ºE.

Well C4 bottom

Site C4 bottom is the base of the east facing slope on the Helmer's Ridge at an elevation of 260m (65º09'51.5"N, 147º30'00.2"W). The site consists of two wells, C41 (100' deep) and C42 (68' deep), located 5m apart, parallel to the slope. C41 is for the ground temperature observation. C42 is for the ground water observation purpose. The vegetation at the site consists of open black spruce forest (*Picea mariana*) and with 30cm organic mat of feather mosses and sphagnum. The site slopes 1º to 90ºE.

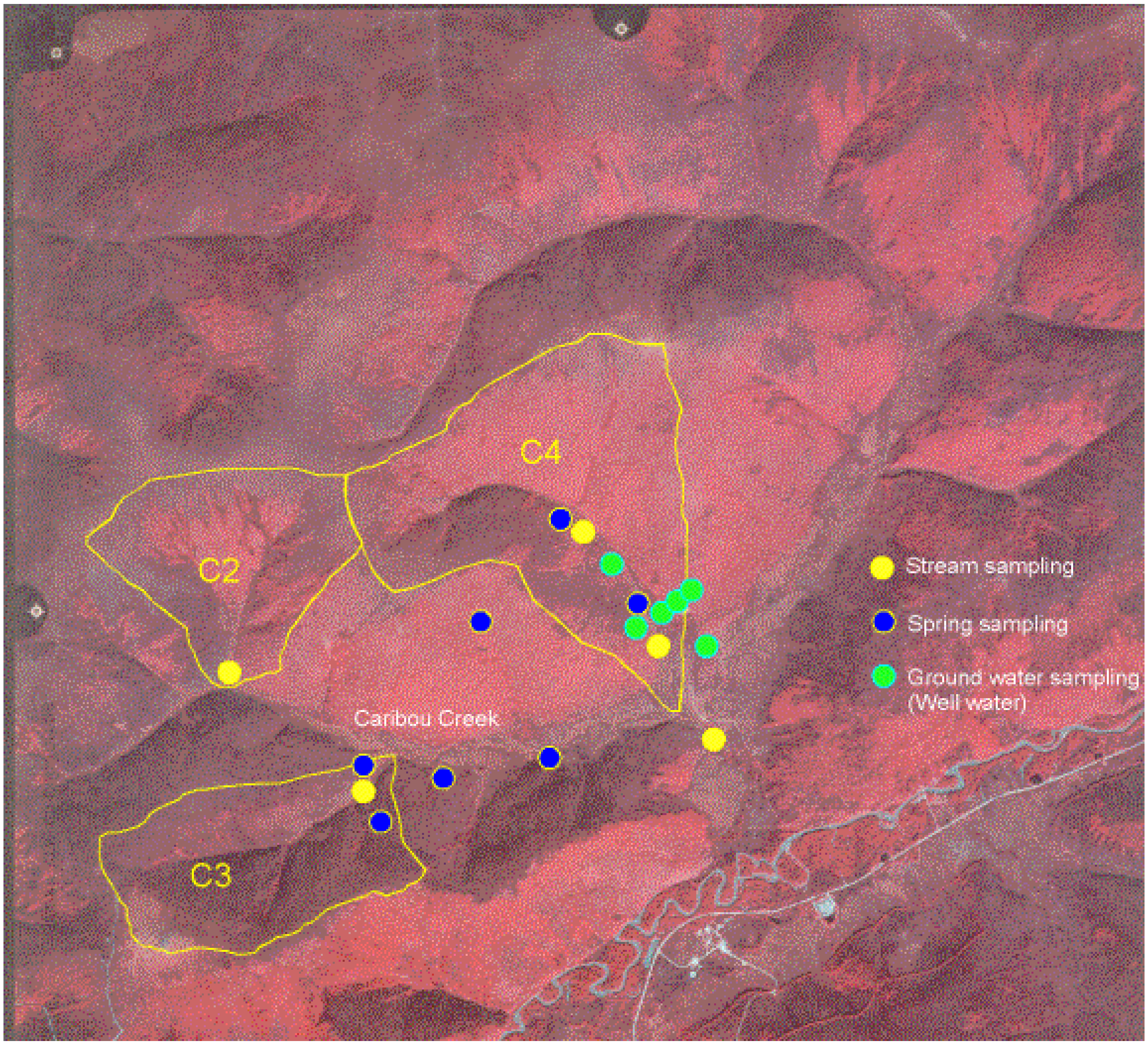

Figure 1. CPCRW indicating stream, spring and groundwater sampling sites.

Well Cabin

Site Cabin is almost bottom of the south facing slope on the Caribou Peak at an elevation of 239m (65º09'25"N, 147º29'12"W). The site consists of one well (71' deep) for ground water observation. The vegetation at the site consists of a closed mixed forest community of black spruce, birch and aspen (*Picea mariana*, *Betula papyrifera*, and *Populus tremuloides*) with a closed low shrub layer of *Ledum groenlandicm* and with 5cm organic mat of feather mosses and sphagnum. The site slopes 5º to 170ºE. No permafrost is found in this site.

4 slope three wells

Three shallow wells are located on the west-facing slope of Caribou Peak. Depth of the wells is less than 30'. The vegetation at the site consists of a closed mixed forest community of black spruce, birch and aspen (*Picea mariana*, *Betula papyrifera*, and

Populus tremuloides) with a closed low shrub layer of *Ledum groenlandicm* and with 5cm organic mat of feather mosses and sphagnum.

Pyrolysis-GC/MS of water samples

Pyrolysis will be conducted with a CDS Model 2500 pyrolyzer and state of the art autosampler in tandem with a gas chromatograph/mass spectrometer (GC/MS). During pyrolysis the sample is heated from a starting temperature of 25 ^{o}C to 700 ^{o}C in 0.1 seconds and held at a constant 700 ^{o}C for 9.9 seconds (see Figure 2). The pyrolysis reactor is mounted on an HP 5890 Series II GC, with a Supelco SPB 35 (35% Ph Me silicon) column, 60 m x 0.25 m x 0.25 µm. The GC interface temperature will be set at 235 ^{o}C. The GC temperature program will be 45 ^{o}C for 5 minutes, 2 ^{o}C /min to 240 ^{o}C and hold for 25 min. The GC is plumbed directly to an HP 5971A Series Mass Selective Detector on electron impact (EI) mode. The MS scans mass units 45 to 650. All mass spectra will be compared to the NBS54K spectral library. Helium serves as a carrier gas at a flow rate of 0.5 cm^3/minute. Each sample will be injected with a split ratio of 1:50. A standard curve will be prepared by pyrolyzing known masses of poly-alpha-methylstyrene.

Expected Results

The fingerprinting technique provides us with generalizations and specifics about the chemical make-up of NOM. As in White and Beyer (1999), we expect to correlate the organic matter in various sample with the probable origin. For example, if the NOM in water from a spring exhibits the same fingerprint as NOM in streamwater samples we would postulate that the two are in direct communication and are derived from water at the same source.

NOM fingerprints will be interpreted on the basis of biochemical class as well as individual compounds for predicting substrate quality. For example, in the figure below, two fingerprints of NOM from Antarctic soil are compared. The two fingerprints are of different soil horizons at the same site with the top fingerprint representing the soil surface. The fingerprinting technique allowed us to identify individual compounds as well as regions (see Figure 2). Once we observed that certain compounds were being preserved or degraded in the depth profile, we identified the individual compounds and proposed a mechanism by which the compounds were transformed/translocated (White and Beyer, 1999).

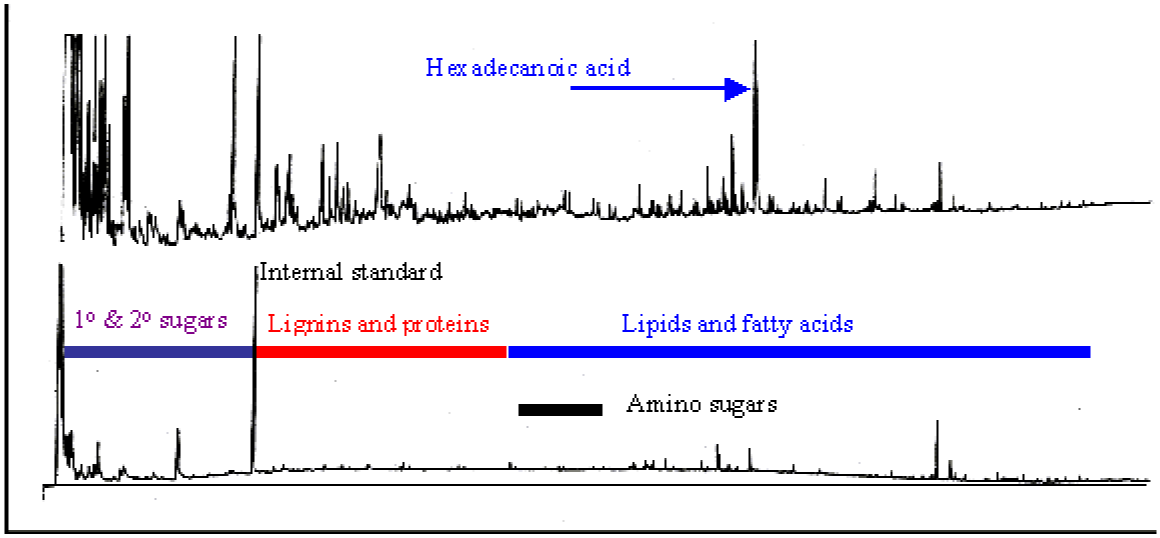

Figure 2. Fingerprints of Antarctic SOM at the ground surface (top) and approximately 1 m below surface (bottom). Examples of individual compounds and biochemical classes are indicated.

Integration and Synthesis

Significance of the proposed research

This research will lend additional evidence as to the origin of organic matter in water from permafrost regions. This information is important to hydrologic research as well as to research on the characteristics organic matter in well water used for drinking. Organic matter in treated drinking water may result in serious degradation of human health.

Integration

This research will compliment ongoing research by Dr. White on organic matter in drinking water. One part of the existing project was to investigate groundwater-surface water interactions in permafrost. Funding of a graduate student through WERC would leverage the existing funding from the EPA. Since no supplies funding is being requested from WERC, EPA funds would be used to purchase supplies needed by the graduate student for sampling and analysis.

This research will also compliment ongoing research by Dr. Yoshikawa on the hydrology of the CPCRW. Drs. White and Yoshikawa expect to submit a proposal to the NSF Earth Systems program to expand this WERC project. While this proposal focuses on 18 sites, the NSF proposal will look at addressing approximately 100 sites including vegetation, soil and soil-water samples. Funding from the WERC will allow us to pilot test our hypotheses.

Data Plan

In order for the data collected to serve the scientific community, the results should be disseminated as efficiently as possible. As such, project results will be recorded on the web page of the UAF Water and Environmental Research Center. Data will be added to the CPCRW CD data set generated by Yoshikawa and Hinzman. In addition, to ensure peer review of the data, one journal publication is planned. The publication will document the collection of samples, pyrolysis fingerprinting of the soils and hydrologic interpretation. The results will be presented in the WERC seminar series.

Timeline and Workplan

The proposed project will last one year and be divided into two phases. The goals, objectives and products of each phase are outlined in Table 1.

Table 1. Phases of Proposed Research Project

Project Phase	**Goals and Objectives**	**Products of Research**
Water sampling	Water sampling will be conducted during the period June-July. It is anticipated that all sites will be sampled three times during the summer.	
Pyrolysis-GC/MS analysis	The NOM in water samples will be fingerprinted by pyrolysis-GC/MS and statistically cross-correlated based on the chemical composition of the organic matter.	Published journal article in peer-reviewed literature on the verification of fingerprinting method. A description of the organic matter characteristics that allow us to predict hydrologic flow paths in permafrost Project description and results will be made available on the LTER and Water and Environmental Research Center websites (**http://www.uaf.edu/water/)**

References

White, D.M. and Beyer, L., (1999) Pyrolysis-GC/MS and GC/FID of three Antarctic soils, *Journal of Analytical and Applied Pyrolysis*, Vol. 50, pp. 63-76.